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Thermal decomposition properties and compatibility of CL-20 with binders HTPB, PBAN, GAP and polyNIMMO

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Abstract The compatibility of filler 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) with rocket propellant binders: hydroxyl-terminated polybutadiene (HTPB), butadiene-acrylonitrile-acrylic acid terpolymer (PBAN), glycidyl azide polymer (GAP) and poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO), has been examined. The compatibility of the compounds has been tested in accordance with the STANAG 4147 standard and its modification consisting in the change of the heating rate. As it arises from STANAG 4147 standard criterion, CL-20 is not compatible with polyNIMMO, PBAN and GAP and possibly incompatible with HTPB. Changes of relative position of peaks between measurements performed in hermetical pans and pans with a pinhole and with different heating rate were observed. In case of polyNIMMO and HTPB, changes of measurement parameters lead to estimated compatibility change. The analysis of the thermal decomposition of CL-20 revealed that it is a two-phase process. The first phase is associated with decomposition in solid phase; the second phase is associated with decomposition of volatile intermediate products of CL-20 decomposition. Due to the complex process of decomposition of tested samples, the apparent activation energy was used for the assessment of the compatibility. The apparent activation energy of the initial phase of decomposition CL-20 and its mixtures with binders are compatible with one another within the limits of measurement error. Results of measurement of apparent activation energy do not indicate a destabilizing effect of binders on the initial phase of decomposition of CL-20.

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Introduction

Binders such as hydroxyl-terminated polybutadiene (HTPB), butadiene-acrylonitrile-acrylic acid terpolymer (PBAN), glycidyl azide polymer (GAP) and poly(3-nitratomethyl-3-methyloxetane) (polyNIMMO) are substances added to rocket propellants in purpose to bond solid components of propellant and to give it the appropriate mechanical properties. Fast burning rocket propellants, with a high specific impulse, very commonly contain ammonium chlorate(VII) (AP) and aluminium (Al) in addition to binders in its composition [1]. The main disadvantage of such propellants is the formation of signature during engine operation, which allows easy detection of a flying rocket and its launch site. The signature can be reduced by the elimination of Al and reduction of AP. These components can be replaced with a high-energy filler such as 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20). In order to ensure the safe storage and use of rockets, propellant components should be compatible with each other [2–8]. The NATO Standardization Agency recommends determination of compatibility at heating rate of 2 K min^{-1} [7]. There are some descriptions found in the literature which concern the compatibility examinations performed at heating rate of 10 K min^{-1} [2, 8]. However, the best influence visibility of one substance on thermal decomposition of the other can be obtained by analysing changes of kinetic parameters of decomposition reaction [3, 5, 6]. In accordance with the recommendations of International Confederation for Thermal Analysis and Calorimetry (ICTAC), full kinetic analysis should be based on the determination of the activation

energy, pre-exponential factor and reaction model [9]. During the decomposition of high-energy materials, and especially a multicomponent mixture, many parallel and successive reactions can proceed [5, 9]. Determined kinetic parameters are the result of all the processes taking place during the decomposition of the sample. Therefore, it is difficult to determine the model of such a decomposition reaction. Without assuming the reaction model, it is impossible to determine the pre-exponential factor. Recommended isoconversional methods allow estimating the activation energy without assuming any reaction model. For practical reasons, in this study, the effect of one compound on the thermal degradation of the second compound in the mixture was analysed by changes in the activation energy. Due to the complex process of decomposition of tested samples, determined parameter in the later work is called the apparent activation energy $_{a}$Ea. Uncontrolled decomposition of a high-energy mixture, caused for example by the lack of compatibility, may lead to the thermal explosion [10]. Such an event can occur even in low degrees of conversion [11]. For this reason, the influence of ingredients on the changes in the apparent activation energy was analysed for the initial level of conversion.

The following paper presents the study of the compatibility of CL-20 with selected binders of heterogeneous rocket propellants. The compatibility was determined in hermetic pans and in pans with a pinhole at two different heating rates: 2 and 10 K min^{-1}. The influence of the measurement conditions on the determined compatibility was analysed. The apparent activation energy of decomposition reaction of the examined mixtures and their components was determined and compared depending on the degree of conversion. The results of compatibility of the studied systems determined by comparison of peaks were compared with the results of compatibility determined by comparison of the activation energy changes.

Experimental

Materials

εCL-20 (impact sensitivity about 4 J) with the chemical purity of 98 % and the polymorphic purity >95 % was synthesized in the Department of High Energetic Materials of the Faculty of Chemistry at the Technological University of Warsaw, Poland. GAP and polyNIMMO with the chemical purity of 98 % were synthesized in the Industrial Chemistry Research Institute, Poland. HTPB was synthesized at the Industrial Chemistry Research Institute, Poland, Mn = 2,500, Mw = 4,000, OH = 1.2 meq g^{-1}, water content max. 0.2 %. PBAN is manufactured by the Research and Development Centre of Rubber and Vinyl Plastics (OBR KiTW) in Oświęcim, Mn 2230. Binary mixtures used in the study were obtained by grinding components in an agate mortar at the mass ratio of 1:1.

Experimental techniques

The measurements were carried out using the Differential Scanning Calorimeters Pyris1 made by PerkinElmer and the Q2000 made by TA Instruments. Measuring conditions were as follows:

- heating rate of $\beta = 0.5$, 1, 2, 5, 7, 10 and 15 K min^{-1},
- measurements were carried out in hermetic pans, sample mass 0.5 ± 0.1 mg,
- measurements were carried out in hermetic pans with a 0.7-mm pinhole, sample mass 1.0 ± 0.1 mg, single components, mixture 2.0 ± 0.1 mg.

Compatibility

The compatibility was determined according to the method specified in STANAG 4147 [7]. The measurements were carried out for samples of the tested substances with a mass of 1 ± 0.1 mg and 1:1 (w/w) mixture with a mass of 2 ± 0.1 mg in pans with a pinhole, at a heating rate of $\beta = 2$ K min^{-1}. Decomposition peak minimum temperatures of CL-20 (T_a) were compared with values obtained for the mixture of CL-20 with other ingredient (T_{ab}). If T_{ab} of mixture decomposition is more than 20 K lower in relation to T_a (CL-20), then CL-20 is incompatible with this other ingredient. If the shift in the direction of lower temperatures is in the range of 4–20 K, then CL-20 is uncertainly compatible with the other ingredient and it demands further investigation. CL-20 is compatible with the analysed ingredient when T_{ab} is maximum 4 K lower than CL-20 decomposition temperature T_a.

Kinetic parameter calculation methods

Kinetic parameters of the decomposition of the studied systems were determined by using the program Thermokinetics 3.1 NETZSCH. The measurements were carried out at different the heating rate ($\beta = 0.5$, 1, 2, 5, 7, 10 and 15 K min^{-1}) in hermetic pans. In accordance with the recommendations of ICTAC, the apparent activation energy $_{a}$Ea was determined by Friedman's isoconversional method [9, 12].

Results and discussion

The analysis of thermal decomposition of HTPB, PBAN, GAP, polyNIMMO, CL-20 samples and binder mixtures of

CL-20 was conducted. The measurements were carried out in accordance with STANAG 4147 [7]. Modification consisting in the heating rate change (from $\beta = 2$ to $\beta = 10$ K min^{-1}) was also applied. It was used by some authors in the past [2, 8]. Exemplary studies of CL-20 with polyNIMMO, with the use of methods discussed above, are presented in Figs. 1–4.

Figure 1 shows the DSC curves of the thermal decomposition of samples obtained during the measurements performed at the heating rate of $\beta = 2$ K min^{-1} in pans with a pinhole. These conditions are in accordance with STANAG 4147 [7]. The temperature of CL-20 decomposition peak minimum equals 500 K, while this value for the 1:1 (w/w) polyNIMMO/CL-20 mixture $T_{ab} = 474$ K. The temperature of mixture decomposition peak minimum T_{ab} is then 26 K lower than T_a temperature which testifies to the incompatibility of CL-20 to polyNIMMO according to STANAG 4147 standard.

Figure 2 shows the measurements performed in hermetic pans at a heating rate of $\beta = 2$ K min^{-1}. The temperature of CL-20 decomposition peak minimum equals 499 K, while this value for the 1:1 (w/w) polyNIMMO/CL-20 mixture $T_{ab} = 474$ K. The temperature of mixture decomposition peak minimum T_{ab} is then 25 K lower than T_a temperature which testifies to the incompatibility of CL-20 to polyNIMMO according to STANAG 4147 standard. The use of hermetic pans caused a change in shape of decomposition peak of CL-20. The two-phase nature of the decomposition process is clearly visible. This indicates that intermediate volatile products are formed during decomposition of CL-20.

Figure 3 shows the measurements performed at the heating rate of $\beta = 10$ K min^{-1} in pans with a pinhole. This method differs from the one proposed in STANAG 4147 (Fig. 1) due to the change of heating rate from $\beta = 2$ to $\beta = 10$ K min^{-1}. The temperature of CL-20 decomposition peak minimum equals 505 K, while this value for the 1:1 (w/w) polyNIMMO/CL-20 mixture $T_{ab} = 486$ K. The temperature of T_{ab} is then 19 K lower than T_a temperature. According to the STANAG 4147 standard, CL-20 is then uncertainly compatible with polyNIMMO. The increase of the heating rate from $\beta = 2$ to $\beta = 10$ K min^{-1} caused the change of compatibility analysis result of CL-20 to polyNIMMO and the change of CL-20 decomposition peak shape. Also in this case, the two-phase nature of decomposition is visible.

Figure 4 shows the measurements performed in hermetic pans at the heating rate of $\beta = 10$ K min^{-1}. This method differs from the method proposed in STANAG 4147 (Fig. 1) with the increase of the heating rate from $\beta = 2$ to $\beta = 10$ K min^{-1}. The temperature of CL-20 decomposition peak minimum equals the 529 K, while for the 1:1 (w/w) polyNIMMO/CL-20 mixture $T_{ab} = 491$ K. The temperature of mixture decomposition peak minimum T_{ab} is then 38 K lower than CL-20 T_a temperature which testifies to the incompatibility of CL-20 to polyNIMMO, according to STANAG 4147 standard. The change of measurement parameters caused the change of the shift of mixture decomposition peak minimum in relation to CL-20 decomposition peak minimum from $T_{ab} - T_a = -38$ K to $T_{ab} - T_a = -19$ K.

Using the four methods described above, compatibility of CL-20 with PBAN, HTPB and GAP has been determined. Table 1 summarizes the results of the compatibility tests.

According to the criterion of STANAG 4147 standard, CL-20 is incompatible with polyNIMMO, PBAN and GAP and possibly incompatible with HTPB. The changes of

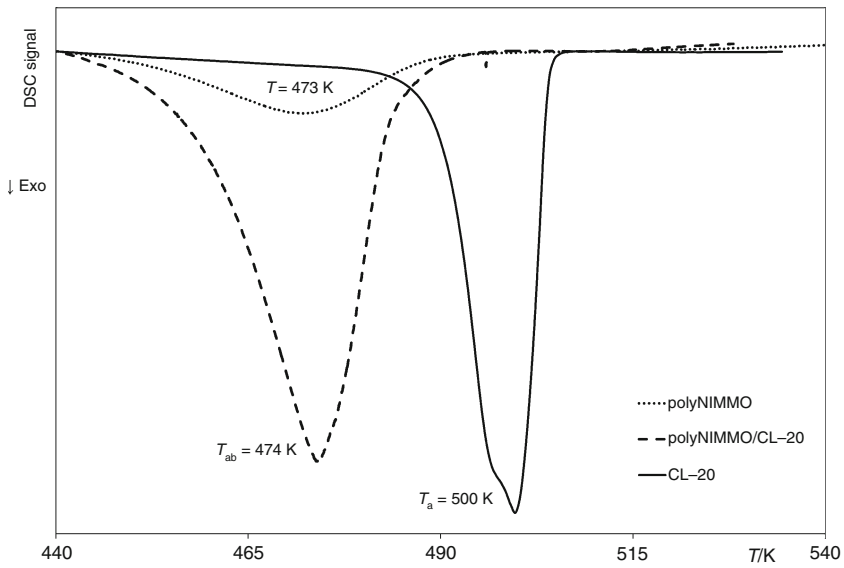

Fig. 1 DSC curves of thermal decomposition of CL-20, and polyNIMMO/CL-20 mixture 1:1 (w/w), $\beta = 2$ K min^{-1}, measurement carried out in a pan with a pinhole

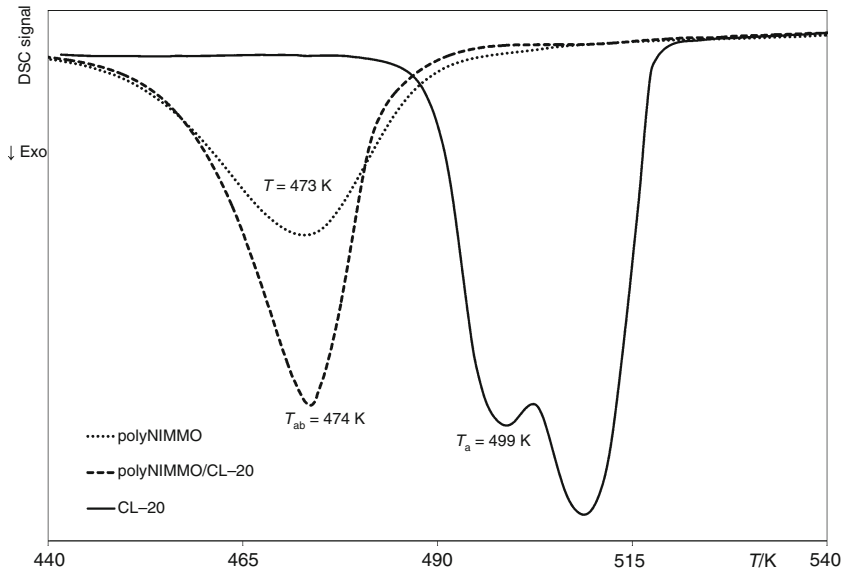

Fig. 2 DSC curves of thermal decomposition of CL-20, and 1:1 (w/w) polyNIMMO/CL-20 mixture, $\beta = 2$ K min^{-1}, measurement carried out in a hermetic pan

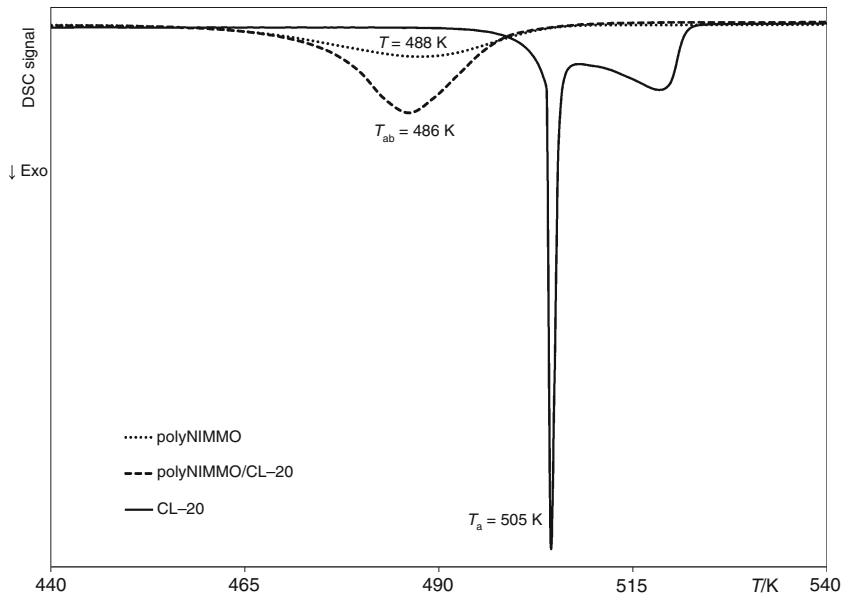

Fig. 3 DSC curves of thermal decomposition of CL-20, and polyNIMMO/CL-20 mixture 1:1 (w/w), $\beta = 10$ K min^{-1}, measurement carried out in a pan with a pinhole

relative peaks positions were observed after pan type changing (from hermetical pan to the pan with a pinhole), but estimated compatibility did not change. The increase of heating rate from $\beta = 2$ to $\beta = 10$ K min^{-1} caused the change of relative peaks positions, which lead to the change of estimated compatibility in case of polyNIMMO and HTPB.

The kinetic parameters were determined with regard to the decomposition of CL-20, polyNIMMO binders, PBAN, HTPB, GAP and their mixtures with CL-20. The series of measurements of the CL-20 decomposition carried out at different heating rates are shown in Fig. 5.

As expected, along with the increase of heating rate, the decomposition process of CL-20 moves in the direction of higher temperatures. At lower heating rates (0.5–7.0 K min^{-1}), two-phase nature of CL-20 decomposition is clearly visible. The two-phase CL-20 decomposition process has already been described in the literature [5, 13]. Figure 6 shows the influence of pan types on the nature of the CL-20 decomposition process for heating rate of 2.0 and 10.0 K min^{-1}.

In the measurements performed at a heating rate of 2.0 K min^{-1}, the first stage of decomposition observed in hermetic pans is consistent with the total decomposition observed in a pan with a pinhole. For this heating rate, the two-phase process is more clear, when measured in a hermetic pan. In the measurements performed at the heating rate of 10.0 K min^{-1}, the second stage of decomposition

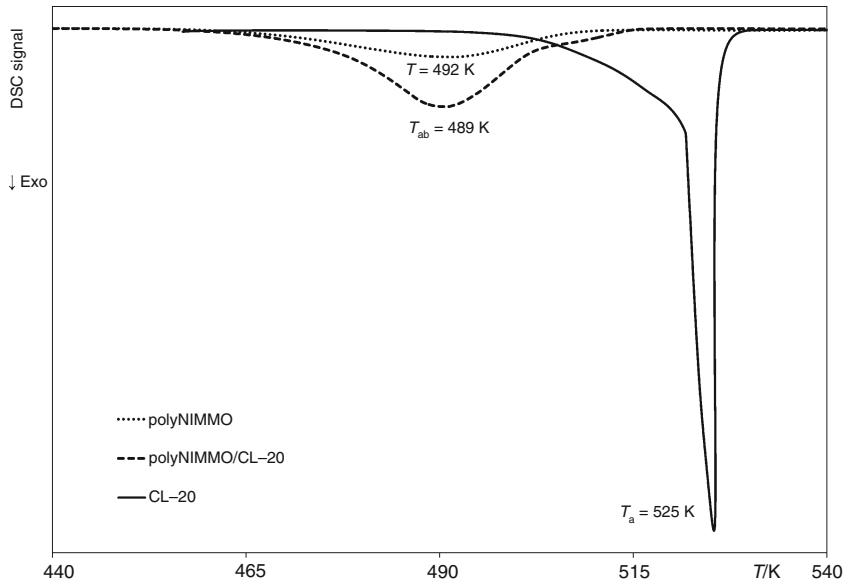

Fig. 4 DSC curves of thermal decomposition of CL-20, polyNIMMO and polyNIMMO/CL-20 mixture 1:1 (w/w), $\beta = 10$ K min^{-1}, measurement carried out in a hermetic pan

Table 1 Results of compatibility tests (C_{ab}) of CL-20 with polyNIMMO, PBAN, HTPB, GAP, determined in the performed measurements in pans with a pinhole and hermetic pans, at a heating rate of $\beta = 2$ and 10/K min^{-1}

CL-20 with	$\beta = 2$/K min^{-1}				$\beta = 10$/K min^{-1}			
	Pans with a pinhole		Hermetic pans		Pans with a pinhole		Hermetic pans	
	$T_{ab} - T_a$/K	C_{ab}	$T_{ab} - T_a$/K	C_{ab}	$T_{ab} - T_a$/K	C_{ab}	$T_{ab} - T_a$/K	C_{ab}
polyNIMMO	−26	–	−25	–	−19	±	−38	–
PBAN	−30	–	−27	–	−29	–	−33	–
HTPB	−20	±	−18	±	−31	–	−27	–
GAP	−31	–	−48	–	−31	–	−36	–

T_a—minimum peak decomposition temperature of less stable substances, T_{ab}—minimum peak decomposition temperature of mixture, "+"—compatible, "±"—possible incompatibility, "−"—not compatible

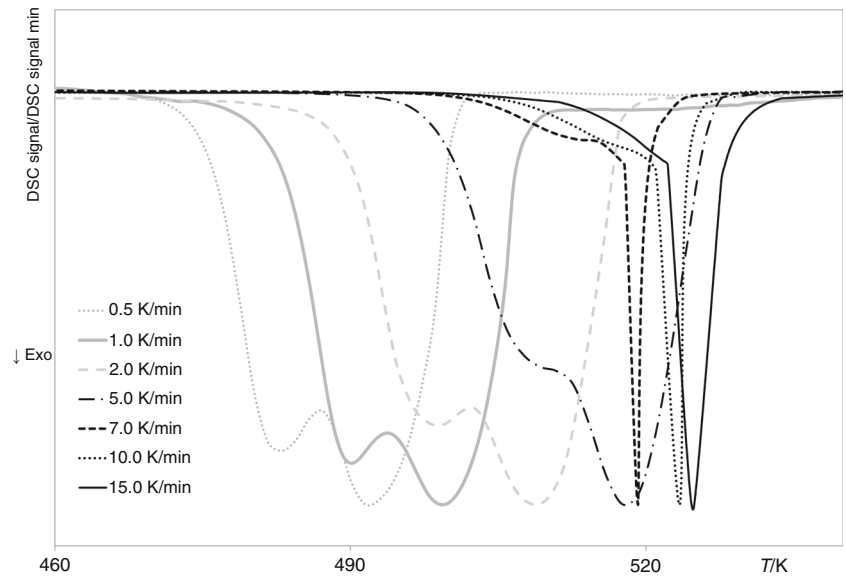

Fig. 5 DSC curves of the thermal decomposition of CL-20 carried out at different heating rates

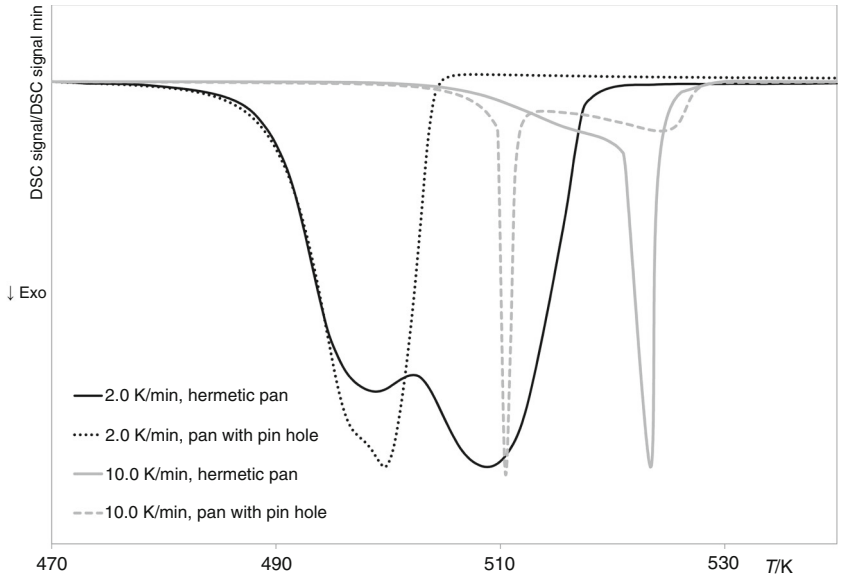

Fig. 6 DSC curves of the thermal decomposition of CL-20 carried out in hermetic pans with a pinhole, with heating rates of 2.0 and 10.0 K min^{-1}

observed in a pan with a pinhole is consistent with the total decomposition observed in a hermetic pan. For this heating rate, the two-phase process is more clear, when measured in a pan with a pinhole. The observed compliance indicates that during the first phase, mostly decomposition of solid material occurs [5], and during the second phase, mostly decomposition of volatile intermediate products occurs. Sample decomposition effect may be overlaid with CL-20 sublimation process, which is described in the literature [13]. This process might take place in hermetical pans, but its participation in total endothermic effect will be very small because of high pressure in pan during the measurement. Two-stage decomposition in hermetical pan is connected with CL-20 and its intermediate degradation products decomposition. The lack of the second, clearly marked decomposition stage during the measurement performed with heating rate 2.0 K min^{-1} in the pan with hole indicates that volatile decomposition products abandoned the pan and the sublimation process participation is small.

The apparent activation energy and the pre-exponential factor with regard to the degree of conversion of the CL-20 decomposition for the measurements performed in hermetic pans are shown in Fig. 7.

In some papers, single values of the activation energy of the decomposition reaction of CL-20 are given [3, 4]. Due to the possible occurrence of many parallel and successive reactions during decomposition, as mentioned in the introduction, it is necessary to analyse the dependence of changes in the activation energy with regard to the degree of conversion [9]. According to Fig. 7, major changes in the apparent activation energy were shown, which are associated with the two-phase nature of the CL-20 decomposition process. For the degree of conversion, 0.02–0.15, the mean apparent activation energy of ${}_{a}Ea = 168 \pm 7$ kJ mol^{-1} was determined, it is a value close to the literature data pointing to 161 [3] and 166 kJ mol^{-1} [5]. For the degree of conversion of $0.15 \leq \alpha \leq 0.50$, the apparent activation energy increases from 165 ± 7 to 296 ± 32 kJ mol^{-1}. It is due to the overlap of the first and second phase of the decomposition reaction. For the degree of conversion of $0.50 \leq \alpha \leq 0.80$, the apparent activation energy has a constant value typical for the second phase of decomposition. Within this range, the degree of conversion of the mean value of the apparent activation energy is ${}_{a}Ea = 295 \pm 36$ kJ mol^{-1}. Similar changes and the value of the activation energy were described in the literature [14]. The apparent activation energy ${}_{a}Ea$ of the decomposition reaction of CL-20, polyNIMMO, PBAN and mixtures of polyNIMMO/CL-20, PBAN/CL-20, HTPB/CL-20 and GAP/CL-20 was determined. The apparent activation energy of the decomposition of HTPB was not determined due to the lack of visible exothermic decomposition of the sample during the performed measurement tests. The results are shown in Table 2.

The apparent activation energies of CL-20 and its mixtures with binders, determined for the initial decomposition stage ($0.05 \leq \alpha \leq 0.15$), are compatible with each other within the limits of measurement error. The results do not indicate a destabilizing effect of polyNIMMO, PBAN, HTPB or GAP on the initial stage of the CL-20 decomposition. Significant reduction of the apparent activation energy by the binder in the second phase of the CL-20 decomposition is visible. This effect was observed in the analysis of compatibility based on the minimum decomposition peak. Reduction of the apparent activation energy of the second decomposition stage of CL-20 shows the influence of the intermediate reaction products on binders. This influence may be due to dissolution of volatile intermediate products of decomposition CL-20 in the binders or

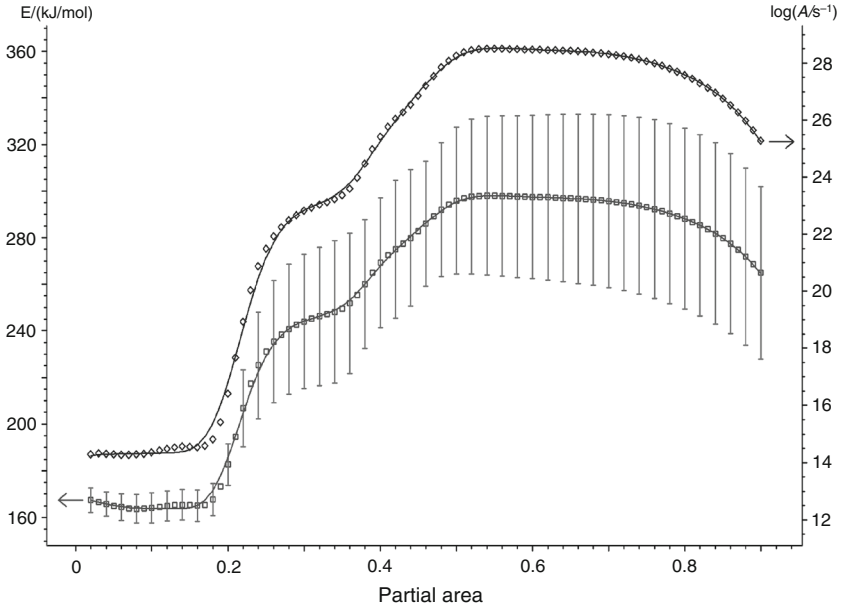

Fig. 7 Changes in the value of the apparent activation energy and the pre-exponential factor of the CL-20 decomposition with regard to the degree of conversion

Table 2 Apparent activation energy $_{a}$Ea of the decomposition reaction of CL-20, polyNIMMO, PBAN and mixtures of polyNIMMO/CL-20, PBAN/CL-20, HTPB/CL-20 and GAP/CL-20

α Reacted	CL-20	PolyNIMMO	PolyNIMMO/CL-20	PBAN	PBAN/CL-20	HTPB/CL-20	GAP	GAP/CL-20
The apparent activation energy $_{a}$Ea/kJ mol^{-1}								
0.02	167 ± 6	164 ± 3	159 ± 6	76 ± 25	175 ± 12	169 ± 8	175 ± 17	134 ± 7
0.05	165 ± 6	168 ± 3	164 ± 3	76 ± 18	174 ± 13	163 ± 5	160 ± 6	146 ± 8
0.10	164 ± 7	169 ± 3	166 ± 3	78 ± 14	170 ± 13	159 ± 3	153 ± 2	157 ± 9
0.15	165 ± 7	168 ± 3	168 ± 3	88 ± 9	168 ± 13	158 ± 3	152 ± 2	156 ± 8
0.20	183 ± 9	167 ± 3	170 ± 4	91 ± 9	167 ± 11	158 ± 3	152 ± 2	153 ± 7
0.25	231 ± 25	166 ± 4	173 ± 6	90 ± 9	166 ± 10	159 ± 3	152 ± 2	153 ± 8
0.30	244 ± 29	165 ± 4	175 ± 7	87 ± 9	164 ± 9	160 ± 4	153 ± 2	154 ± 8
0.35	249 ± 31	164 ± 4	176 ± 9	95 ± 8	162 ± 9	161 ± 8	153 ± 2	156 ± 8
0.40	269 ± 28	163 ± 4	176 ± 10	99 ± 7	160 ± 9	164 ± 12	153 ± 2	156 ± 7
0.45	283 ± 28	162 ± 5	174 ± 11	93 ± 8	158 ± 10	168 ± 16	153 ± 2	153 ± 6
0.50	296 ± 32	161 ± 5	171 ± 13	90 ± 9	156 ± 12	174 ± 21	152 ± 2	146 ± 6
0.55	298 ± 35	160 ± 6	166 ± 14	89 ± 9	155 ± 14	181 ± 25	152 ± 2	134 ± 5
0.60	297 ± 35	159 ± 7	162 ± 15	88 ± 10	155 ± 16	189 ± 31	151 ± 2	104 ± 6
0.65	297 ± 37	158 ± 8	159 ± 16	88 ± 8	157 ± 18	191 ± 38	151 ± 2	47 ± 10
0.70	296 ± 38	156 ± 10	157 ± 18	86 ± 6	160 ± 21	158 ± 39	150 ± 2	62 ± 17
0.75	293 ± 39	151 ± 12	155 ± 21	83 ± 3	168 ± 26	126 ± 25	148 ± 2	92 ± 26
0.80	288 ± 39	141 ± 17	152 ± 27	79 ± 4	183 ± 37	144 ± 14	147 ± 2	132 ± 8
0.85	280 ± 39	106 ± 32	150 ± 38	75 ± 8	190 ± 66	178 ± 13	145 ± 1	151 ± 2
0.90	265 ± 37	29 ± 36	118 ± 59	71 ± 11	120 ± 70	189 ± 19	143 ± 1	147 ± 2
The average apparent activation energy $_{a}$Ea/kJ mol^{-1}								
0.02–0.15	165 ± 7	167 ± 3	164 ± 4	80 ± 17	172 ± 13	162 ± 5	160 ± 7	148 ± 8
0.50–0.80	295 ± 36	155 ± 9	160 ± 18	86 ± 7	162 ± 21	166 ± 28	150 ± 2	102 ± 11

a physical separation of the CL-20 phase from the gas phase, ultimately leading to an increase in concentration of autocatalytic degradation products [15]. The analysis of activation energy changes at the initial stage of the decomposition does not confirm the influence of binders on polymorphic and thermal stability of CL-20 in polymers,

described in the literature [2, 3, 6, 16–18]. It is connected with other conditions of performed experiments as well as with the fact that in the part of papers the minimum of decomposition peak was the analysed parameter. Also the content of impurities in the sample influences the polymorphic and thermal stability of CL-20 [13, 19].

The obtained results confirm that the determination of the compatibility based on the decomposition peak minimum has a number of drawbacks. First of all, the analysis of the decomposition peak minimum, which is observed for a large degree of conversion, for first-order $\alpha = 0.61$ [20]. Analysis of the system properties with large degree of conversion refers to a mixture of the parent compound and degradation products (in the case of one-phase reaction) or a mixture containing only traces of the parent compound (in the case of multi-stage reaction, for example, trinitrotoluene decomposition, where 94 % of the material reacts until 64 % of thermal effect gets released [20]). For security reasons, we are interested in the properties of the parent compound. In addition, measurements made in pans with a pinhole are subjected to error due to the evaporation of the test substance or intermediate products of decomposition. The study of the thermal compatibility stability should be based on samples of high mass and performed in the lowest temperature [21, 22].

Conclusions

Compatibility of CL-20 with polyNIMMO, PBAN, HTPB and GAP was estimated according to STANAG 4147 standard and its modification consisting in the change of heating rate from $\beta = 2$ to $\beta = 10$ K min^{-1}. As it arises from STANAG 4147 standard criterion, CL-20 is not compatible with polyNIMMO, PBAN and GAP and possibly incompatible with HTPB. Changes of relative position of peaks between measurements performed in hermetical pans and pans with a pinhole and with different heating rate were observed. In case of polyNIMMO and HTPB, changes of measurement parameters lead to compatibility change.

Thermal decomposition of CL-20 is a two-phase process. The first phase is visible for the degree of conversion of $0.02 \leq \alpha \leq 0.15$ with the mean apparent activation energy of ${}_{a}Ea = 168 \pm 7$ kJ mol^{-1}. For the degree of conversion of $0.15 \leq \alpha \leq 0.50$, we observe the overlap of the first and second phase of the decomposition reaction and the increase of the apparent activation energy from 165 ± 7 to 296 ± 32 kJ mol^{-1}. For the degree of conversion of $\alpha = 0.8$, the apparent activation energy has a constant value of ${}_{a}Ea = 295 \pm 36$ kJ mol^{-1} typical for the second phase of decomposition. The results obtained indicate during the first phase, mostly decomposition of solid material occurs, and during the second phase, mostly decomposition of volatile intermediate products occurs. The apparent activation energies of the initial stage of decomposition ($0.05 \leq \alpha \leq 0.15$) of CL-20 and its mixtures with binders are compatible with each other within the limits of measurement error. The results obtained do not indicate that polyNIMMO, PBAN, HTPB and GAP destabilize the initial stage of the CL-20 decomposition. The tested binders significantly reduce the apparent activation energy of the second stage of the CL-20 decomposition, which demonstrates their influence on indirect products of the CL-20 decomposition. Uncontrolled decomposition of a high-energy mixture, caused by the lack of compatibility, may lead to thermal explosion even at low degrees of conversion. For this reason, the compatibility test should be based on the analysis of the initial stage of decomposition.

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